



Enhancing uranium solubilization in soils by citrate, EDTA, and EDDS chelating amendments

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ABSTRACT

A systematic study was made of the effects of three soil amendments on the solubilization of uranium from a granitic soil. The aim was to optimize solubilization so as to enhance bioavailability for the purposes of remediation. The three amendments tested were with citrate, EDTA, and EDDS as chelating agents. The effects of pH, chelator concentration, and leaching time were studied. The most important factor in uranium solubilization was found to be the pH. In the absence of chelating agents, the greatest solubilization was obtained for alkaline conditions, with values representing about 15% of the total uranium activity in the bulk soil. There were major differences in uranium solubilization between the different amendments. The citrate treatment was the most efficient at acidic pH, particularly with the greatest concentration of citrate tested (50 mmol kg⁻¹) after 6 days of treatment. Under these conditions, the uranium concentration in solution was greater by a factor of 356 than in the control suspension, and represented some 63% of the uranium concentration in the bulk soil. Under alkaline conditions, the EDTA and EDDS treatments gave the greatest uranium activity concentrations in solution, but these concentrations were much lower than those with the citrate amendment, and were not very different from the control results. The uranium extraction yield with EDDS amendment was greater than with EDTA.

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1. Introduction

It is conventional farming practice to treat soils with chemicals in order to increase plant uptake of essential elements and nutritional compounds. In some situations, these same treatments can be used to enhance the soil-to-plant transfer of non-essential and toxic elements such as heavy metals or radionuclides [1].

For the soil-to-plant transfer process to occur the element must be available to the plant, i.e., it must be in the soil solution [2]. Furthermore, the speciation of the element in the soil solution must be suitable for incorporation by the plant, i.e., it must be bioavailable [3]. Soil-to-plant transfer is thus a complex process that depends on the characteristics of the soil and the plant. One of the most important factors of this environment is the pH, because it determines the speciation of the element of concern [4]. The addition of certain chelating reagents can improve the release of elements from the soil matrix into the soil solution, and hence make them more available to plants. Chelation of toxic elements may also make them more bioavailable, and enhance their translocation from the roots to the aerial parts of the plant [5].

It has been established that enhancements in the passage of uranium from the soil matrix to the soil solution also increases the transfer of the element to the plants [6,7]. While the use of different chelating agents targeted at heavy metals has been studied extensively [8–12], there have been fewer works considering the effect on natural radionuclides such as uranium [6,7,13–15]. These few studies have, however, shown that bi- and tri-dentate chelating agents give the best results for uranium. In particular, the use of oxalates or citrates, whether as acids or anions, have given high values of uranium solubilization in soils [16]. Successful results with citrate have been reported by various groups of workers [6,7,13]. EDTA also has been extensively used for soil amendment, not only in normal farming practice but also to precondition soils for remediation purposes [17,18]. But in the case of uranium, EDTA has been tested by various workers with the results being unsuccessful [13,15]. Other chelators, such as EDDS, have been applied to heavy metal remediation because of their greater degradability and environmental friendliness relative to the longer-lived EDTA [12]. Nonetheless, the application of EDDS to radionuclides has rarely been studied [15].

The aim of the present work was to gain detailed knowledge on the release of uranium from the soil matrix into solution in a suspension of a granitic soil dosed with citrate, EDTA (ethylenediaminetetraacetic acid), or EDDS ([S,S]-stereo-isomer of

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Table 1
Properties of the soil sample.

Soil parameter	Values	Reference
Fraction < 2 mm	78.3%	
Texture		
Sand	71.9%	
Silt	19.85%	[21]
Clay	8.25%	
Field capacity	27.5%	[22]
Loss on ignition (LOI)	4.93%	[21]
Organic matter	3.47%	[23]
pH	5.58	[21]
Soil moisture	12.3%	[21]
CEC	1.4 cmol kg ⁻¹	[24]
Ca ²⁺	386 mg kg ⁻¹	
Mg ²⁺	42 mg kg ⁻¹	
K ⁺	104 mg kg ⁻¹	
Available P	80.2 mg kg ⁻¹	[25]
Nitrogen	0.194%	[26]
²³⁸ U	3385 ± 108 Bq kg ⁻¹ (272 ± 9 mg kg ⁻¹)	[27]
²³⁴ U	3652 ± 78 Bq kg ⁻¹ (negligible mass concentration)	[27]

ethylenediaminedisuccinic acid), including the effects of chelator concentration and pH, and the behaviour over time of the system.

The response to amendments with different agents is soil specific. This study forms part of a broader work that deals with the transfer of uranium series radionuclides from granitic soils to selected plants with the aim of understanding which factors, whether characteristic of the soils or of the plants, govern the translocation of these nuclides towards the aerial parts of the plant, i.e., their phytoextraction. The focus is on optimizing phytoextraction as a technique for the remediation of large areas with medium- and low-level uranium contamination.

2. Materials and methods

2.1. Sampling area and soil characterization

The soil sampling was carried out at the “Los Ratones” mine, located in the Region of Extremadura in the south-west of Spain. The mine area that was most affected by mining activities has been well characterized in previous work [19], and the present sampling point was selected to provide a soil with a high activity concentration of natural radionuclides, principally of the ²³⁸U series.

The soil sample was collected from the topsoil layer (to 10 cm depth) with an EJKELKAMP split-tube sampler. It was oven-dried at 80 °C to constant weight, then sieved to a particle size of 2 mm and homogenized. Representative aliquots were carefully selected from the original bulk soil sample [20]. These aliquots were used respectively to determine the activity concentration of natural uranium, and the following physicochemical properties: field capacity, loss on ignition (LOI), moisture content, organic matter, available P and N, cation exchange capacity (CEC), and pH. For the texture analysis, the respective homogenized aliquot was classified using Robinson's pipette method [21] into three categories: sand, silt, and clay. Table 1 lists the results of these analyses.

2.2. Radiochemical methods and measurement techniques

The activity concentrations of the natural uranium isotopes in the bulk soil and leached samples were determined by alpha-spectrometry with PIPS semiconductor detectors. High spectrometric-quality sources were prepared by electrodeposition after the necessary prior radiochemical procedures, as described in the following.

For the determination of ²³⁴U and ²³⁸U activity concentrations in the bulk soil, 0.5 g aliquots of soil were digested in a microwave oven [28]. Chemical separation of the uranium from the 8 M HNO₃ solutions in both types of sample (soil and leachates) was performed by the tri-butyl-phosphate (TBP) method [27]. This was followed by electrodeposition to form the high-resolution alpha sources [29,30]. The tracer used was ²³²U.

The ²³⁸U and ²³⁴U activity concentrations (Bq kg⁻¹) in the bulk soil sample were 3385 ± 108 and 3652 ± 78, respectively (see Table 1). These values were obtained from three replicate analyses.

2.3. The soil pH buffering capacity

The pre-defined initial pH values were set using HCl or KOH reagents for the necessary adjustments. In order to determine the amount of HCl or KOH required to reach the desired pH in the soil, it was necessary to study the soil's buffering capacity. To this end, the following series of experiments were carried out, and then the values of the pH of the different mixtures of soil and acid or alkali solutions were measured daily over 15 days.

For the experiments, 20 g of dry sieved soil were suspended in 40 mL of solution in a 60 mL cylindrical polyethylene bottle. The solution consisted of 20 mL of 10 mM CaCl₂ mixed with different volumes of the acid or alkali reagent (0.06 M KOH or 0.06 M HCl) to reach the desired final molarity. Finally, de-ionized water was added to complete the volume of 40 mL. The bottles were shaken continuously during the experimental period and the entire system was maintained in darkness.

2.4. Leaching tests

To optimize the solubilization of uranium from the soils, three chelating agents were tested: citrate, EDTA, and EDDS. We studied the influence of the initial concentration of chelating agent, of pH, and of test time. In particular, four different concentrations were considered for citrate (5, 10, 25, and 50 mmol kg⁻¹), three for EDTA (0.5, 2.5, and 5 mmol kg⁻¹), and four for EDDS (2, 5, 10, and 15 mmol kg⁻¹). For each agent concentration, different experiments were carried out adjusting the pH value to four different soil pH values. These pH values were restricted to the range of tolerance for plants (pH between 4 and 8). For each chelating agent concentration and pH, four experiments were carried considering different lixiviation times: 24, 48, 96, and 144 h. Also a group of samples were tested without chelating agent as controls.

In each test, 5 g of dry soil was put into a 50-mL glass centrifugation tube. At a first stage in order to attain stability of the pH, 20 mL of a solution with pre-conditioned pH was added to suspend the soil. The solutions were prepared with 12.5 mL of 10 mM CaCl₂, and different volumes of 0.06 M HCl or 0.06 M KOH to reach the pre-defined pH, followed by the addition of de-ionized water to reach 20 mL final volume. The *a priori* selected pH values were 4, 5.5, 6.5, and 8. The amounts of acid or alkali reagents needed to attain these values and the time necessary for stabilization were obtained from the results of the pH buffering experiments. In particular, those experiments established an optimal incubation time of 72 h (see Section 3.1). After this 72 h incubation period, the pH of each sample was measured, and the respective chelating agent was added.

For each of the three chelating agents tested, 5 mL of solution containing the desired amount of agent and pre-conditioned to the selected pH was added to the incubated suspension. The chelating agent concentration ranges (per kg dry-soil) were: 0–50 mmol citrate, 0–5 mmol EDTA, or 0–15 mmol EDDS. The upper limits of these ranges were taken from the results of previous phytotoxicity

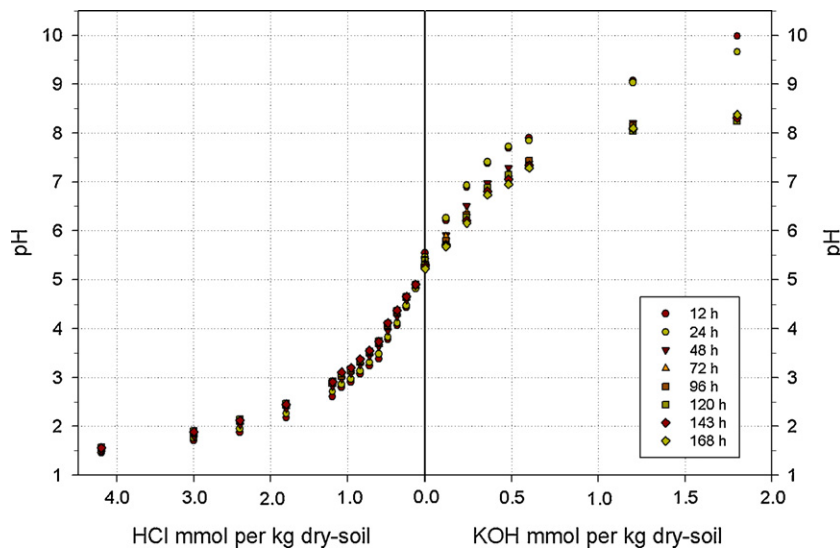


Fig. 1. Variation of soil pH with amount of added reagent (HCl or KOH) and incubation time.

studies for each agent with the plants *Brassica juncea* and *Helianthus annuus* L. [31].

The tubes were again closed with SEPTUM caps and maintained under continuous shaking in the orbital shaker, with the complete system covered with the opaque housing. Measurements of pH were made at 24, 48, 96, and 144 h. The tubes were then centrifuged at 4200 rpm, the supernatant was extracted using a 50-mL plastic syringe, and 20 mL was pumped from the syringe through a 25-mm Swinnex filter holder (MILLIPORE) containing a MILLIPORE AP-40 glass microfibre filter to remove any excess suspended material. These 20 mL aliquots of solution were recovered in polyethylene vials for subsequent assay.

3. Results and discussion

3.1. The soil pH buffering capacity

Fig. 1 shows the variation of the soil pH with different added amounts of acid or alkali reagent (HCl or KOH) and times of incubation. The soil showed little buffering capacity, with major changes in pH even with the addition of small amounts of reagent.

The soil can be considered to be weakly acidic, coherent with its granitic origin and its textural definition as a sandy-loam (see Table 1). The pH stabilization was quite rapid in the acidic zone, being already attained at 48 h. It was somewhat slower in the alkaline zone with stabilization essentially attained by 72 h. Hence, 72 h was taken to be the incubation period required prior to the leaching tests.

There was a slight decrease of pH in the zone above the soil's natural pH. This reflected poor solution of the minerals which provide alkalinity to the soil suspension. The low carbonate content of this soil [32] was consistent with the observed behaviour.

Fig. 2 shows the time behaviour of the soil pH (with time 0 taken to be after the 72 h of incubation) for the different concentrations of chelating agents added to the suspension.

For the citrate treatment (Fig. 2a), there were significant changes in soil pH with a dependence on citrate concentration, test time, and pH value tested. In general the final pH value was slightly higher than the initial value. Major changes in pH have also been reported by Ebbs et al. [13]. Those workers attributed these changes to the degradation of the citrate providing the suspension with an extra concentration of carbonates.

The EDTA treatment (Fig. 2b) led to few changes in the soil pH. The recognized persistence of this chelator [18,33] means that no break-down reactions affect its integrity in the suspension.

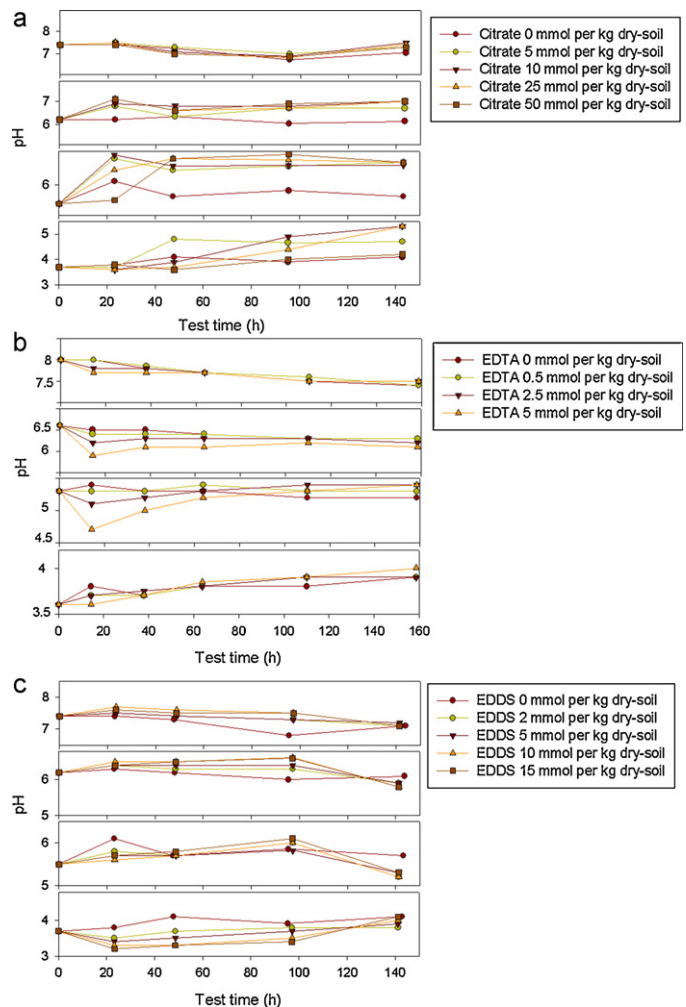


Fig. 2. pH-soil variation with the test time and with concentration of amendments. (a) Citrate; (b) EDTA; (c) EDDS. The test times are considered after 72 h of incubation time.

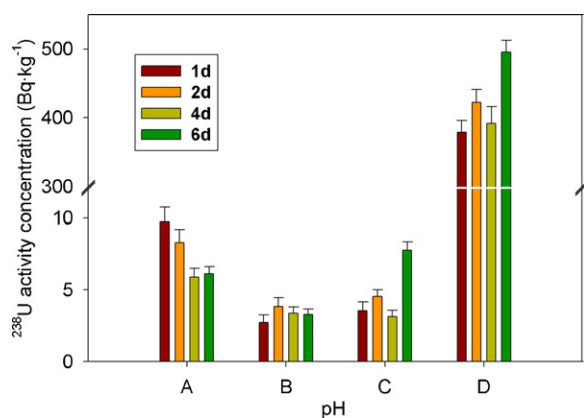


Fig. 3. Variation of the activity concentration of ^{238}U leached without amendment for four test times (1, 2, 4, and 6 days) and four pH ranges (A: 3.7–4.1; B: 5.5–5.8; C: 6.0–6.5; D: 6.8–7.2). The error bars correspond to measurement uncertainties.

The EDDS treatment (Fig. 2c) in general led to more moderate variations until the fourth day. Except for the most acidic series, the other three series showed a marked decrease of pH after 96 h. Duquène et al. [15] also observed in some soils a final decrease of pH following the third day in treatments with EDDS. Tandy et al. [18] found that the degradation of EDDS can be delayed by the formation of stable metallic complexes. This may explain its different effect on the pH relative to citrate during the period studied here.

3.2. Leaching tests

In discussing the results, we shall consider four ranges of pH (in accordance with the results shown in Fig. 2): A (pH 3.7–4.1); B (pH 5.5–5.8); C (pH 6.0–6.5); and D (pH 6.8–7.2).

3.2.1. Treatment without chelating agents

Fig. 3 shows the variation of the activity concentration of ^{238}U in the leachate when no chelating agent was added. Only in the most alkaline condition was there an appreciable liberation of uranium, attaining levels between 400 and 500 Bq kg⁻¹ (between 12% and 15% of the initial bulk soil activity). These concentrations were much greater than that obtained in the more acidic conditions. In the most acidic conditions, there was scarcely any liberation of uranium, even though one should expect the HCl to have some leaching effect [34]. However, the present soil has a low content of uranium associated with the oxide fraction, and a low proportion of clays [32]. But the expected effect was observed when one compares the trend in activity concentrations of the pH ranges A and B: the uranium activity concentrations were always greater in range A, although the differences attenuated with time. At pH's around 4.0, the uranium in solution is predominantly in the form of uranyl ion [13], and the steady decrease in activity observed in this range would be explained by re-adsorption of the uranium in the soil. In the most alkaline range (D), there was an increasing trend of the activity concentration with time. This could be explained by the slow formation of uranium bicarbonate/carbonate complexes following the detachment of organic matter containing uranium [35], but also by the stabilization of uranium–humic complexes in solution which is a slow and highly pH-dependent process [36]. Previous studies [32] have found the soils of this region to be low in carbonate content, and the greatest proportion of uranium to be found associated with organic material. The increasing trend of solubilization of uranium with time is just apparent for the pH range C, but it was with the most alkaline conditions (D) where the greatest activities were observed. The behaviour is compatible with the hypothesis that the most likely is the contribution of

soil organic matter alone, with negligible participation of bicarbonate/carbonate ligands. This will be discussed below (Sections 3.2.2 and 3.2.3), but the formation of uranium bicarbonate/carbonate complexes should be evident with the use of chelators under alkaline conditions, with EDTA or EDDS under these conditions dissolving carbonates in the soil by the formation of complexes with cations such as Ca²⁺ or Mg²⁺ [37]. At this pH, the liberation of carbonate ligands would readily produce stable complexes with uranium [36,38,39]. In such a scenario, one would expect greater uranium concentrations in solution than observed in the absence of chelating agents.

3.2.2. Citrate amendment

Fig. 4 shows the uranium activity concentrations leached with the different citrate concentrations and test times, for the four pH ranges considered. The results showed that the pH greatly influences the uranium solubilization.

The maximum effectiveness of citrate on the solubility of uranium was at acidic pH (range A). The best result corresponded to a concentration of 50 mmol of citrate and after 6 days of treatment. In this case, the uranium concentration in the leachate was a factor of 356 greater than that obtained without citrate amendment, and represented 63% of the uranium concentration in the bulk soil. Ebbs et al. [13] also reported the best results at acidic pH and with the highest citrate concentration that they tested (20 mmol), obtaining 85% of their soil's uranium concentration in the solution. Similarly, other workers [6,14,40] observed that greater citrate concentrations led to increased uranium solubility due to a possible complexation of uranium with citrate. With respect to the dependence on pH, Shahandeh and Hosner [7] found that citrate is more effective in acidic than in alkaline soils, reporting uranium leaching yields of above 50% in all cases, but above 72% when working with acidic soils.

Nonetheless, once solubilized, the uranium will be subject to any changes in the citrate in solution. In some cases, the amount of uranium solubilized diminished over time. The possible explanation is degradation of the citrate present in the soil solution. Indeed, Jones and Darrah [41] give a half life for citrate less than 24 h. Ebbs et al. [13] observed that once the citrate has disappeared, the uranium that had been solubilized with 2 mmol of citrate remained in solution for at least 96 h. This could be due to the slowness of the re-absorption process or because, once in solution, the uranium remains complexed with microorganisms or with carbonate ions that have resulted from the citrate degradation [13]. This last explanation would depend on the pH and the carbonate concentration (i.e., on the initial concentration of citrate). The decrease in solubilized uranium was greater for the lower citrate concentrations at acidic pH values (A), and practically independent of the citrate concentrations from the second day onwards for the pH series B and C, while at alkaline pH (D) there was no such decrease. These results seem to be the opposite of those reported by Ebbs et al. [13] and Duquène et al. [15] who actually observed a greater degradation of citrate at alkaline pH (both of these studies determined the citrate concentrations in solution). In the present study, considering that the citrate degradation is greater at alkaline pH, the uranium could have remained in solution from the action of carbonates originating from that degradation, taking into account that for pH above 7 carbonate–uranyl complexes prevail [42].

Given the capacity for the formation of complexes between citrate and uranium, greater amounts of citrate should solubilize greater amounts of uranium in every range of pH. Indeed, this was observed in Fig. 4 for all the pH ranges studied and initial concentrations of citrate up to 25 mmol per kg dry-soil. Similar results have been reported by other workers [6,13,14,40]. Moreover, Ebbs et al. [13] observed faster citrate degradation at low citrate concentrations (2 mmol versus 10 or 20 mmol), although this degradation of

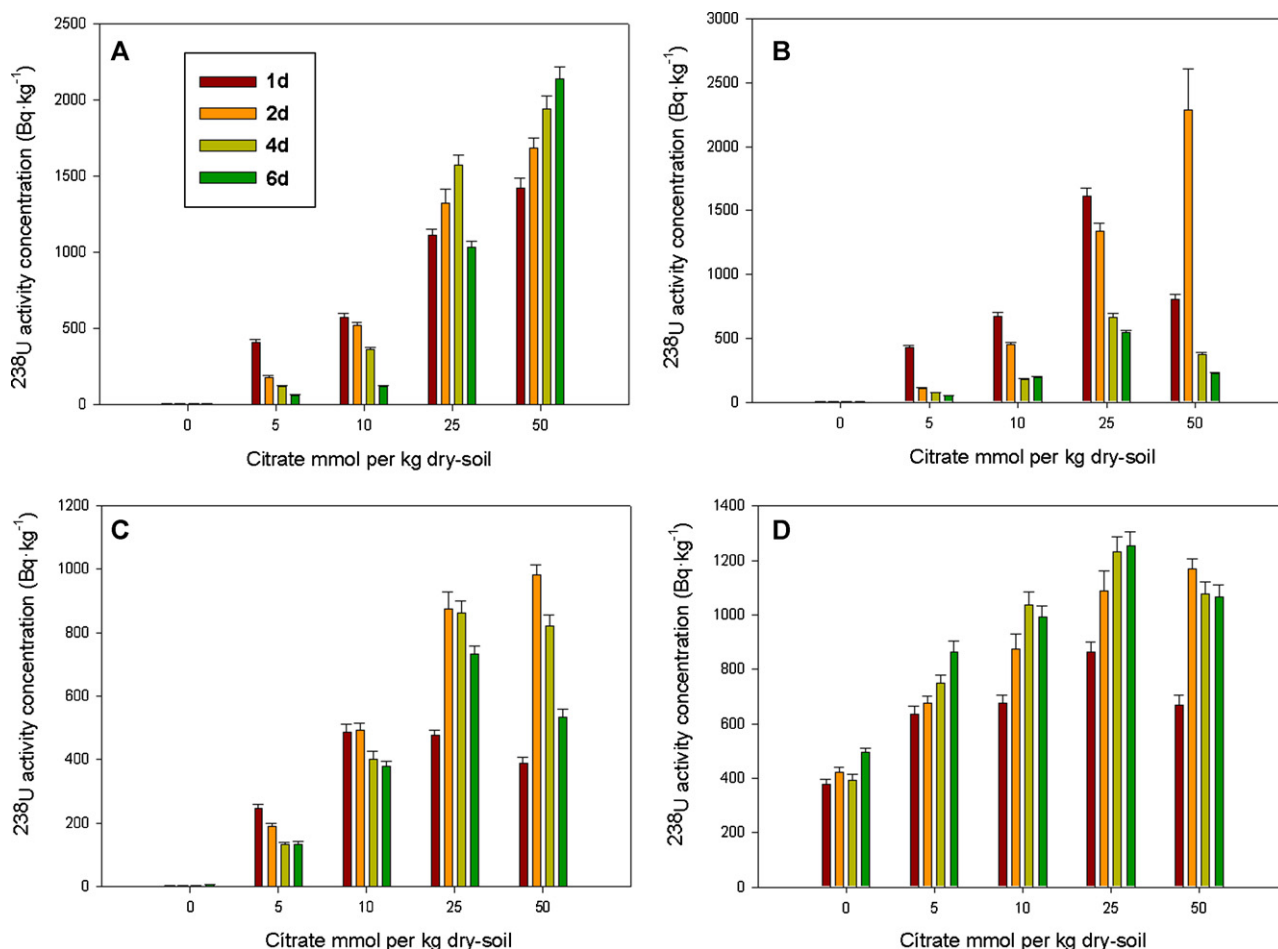


Fig. 4. Variation of the activity concentration of ^{238}U leached with different concentrations of citrate, for four test times and four pH ranges (as in Fig. 3). The error bars correspond to measurement uncertainties.

the citrate at low concentration does not imply any decrease of the solubilized uranium, which remains in solution. The present results are compatible with those of Ebbs et al. [13] if the pH series A, B, and C, are compared which overall cover a similar pH range, and the initial concentrations of up to 25 mmol per kg dry-soil. In the region of the greatest acidity tested, the concentration of solubilized uranium decreased and re-absorption was faster as the initial concentration of citrate was reduced. The results for this acidic pH series could be explained by the solubilization of other cations (Fe or Al) together with uranium. Some workers [6,15] have found significant correlations of U with Fe or Al in the soil solution after citrate amendment at acidic pH. If the citrate solubilizes the oxides of Fe/Al to which the uranium is partially associated, these cations will compete with uranium for the formation of stable complexes in solution, and thus enhance the re-absorption of uranium. The liberation of Fe and Al has also been observed to rise with time and citrate concentration [13], although uranium desorption from their oxides presents a threshold at pH 4–5 [34].

The results obtained in the most alkaline conditions pointed to saturation of the citrate's complexing capacity above 25 mmol per kg dry-soil. For this pH region (D), the liberation of such cations as Al or Fe is considerably attenuated (threshold at pH 4–5) so that there should be more citrate free for uranium complexation relative to more acidic conditions, and at the same time the uranium associated with oxides is more effectively retained [34]. The liberation of organic matter is, however, enhanced as the medium becomes more alkaline [38]. In this case the solubilized uranium could come mainly from the fraction associated with the organic matter, and

the liberation of this organic material and its associated uranium could reach a maximum at 25 mmol of citrate.

Similar conclusions were found in the pH range C (6.0–6.5). In particular, the addition of 50 mmol did not significantly enhance the solubilization achieved with 25 mmol. However, the time behaviour of the uranium once in solution was quite different in the two cases. While for the most alkaline pH range (D) the solubilized uranium remained in solution for at least the duration of the experiment, for the range C re-adsorption seemed to occur. If citrate degradation leads to carbonates in solution, a greater citrate concentration should result in increased carbonate concentration and hence higher concentrations of uranium in solution. However, this was not observed. Other sources of bicarbonate/carbonate ligands due to action of the citrate on the soil have not been considered. It was noted above (Section 3.1) that this soil is poor in carbonate minerals [32]. Some workers [38] have reported low yields in using citrate to dissolve carbonate minerals as evidenced by very little liberation of Ca, Mg, and K, but they describe a major desorption of soil organic matter at pH's between 6 and 8. This organic matter would be responsible for maintaining the uranium in solution, an effect that would be enhanced with increasing alkalinity.

On the use of citrate amendments for phytoremediation with seedlings, the time can be especially important at low citrate concentrations, principally for pH's corresponding to the ranges A and B, but also for higher concentrations of 25 and 50 mmol kg⁻¹ in the pH range B, in which we observed large variations in the solubilization of uranium [43].

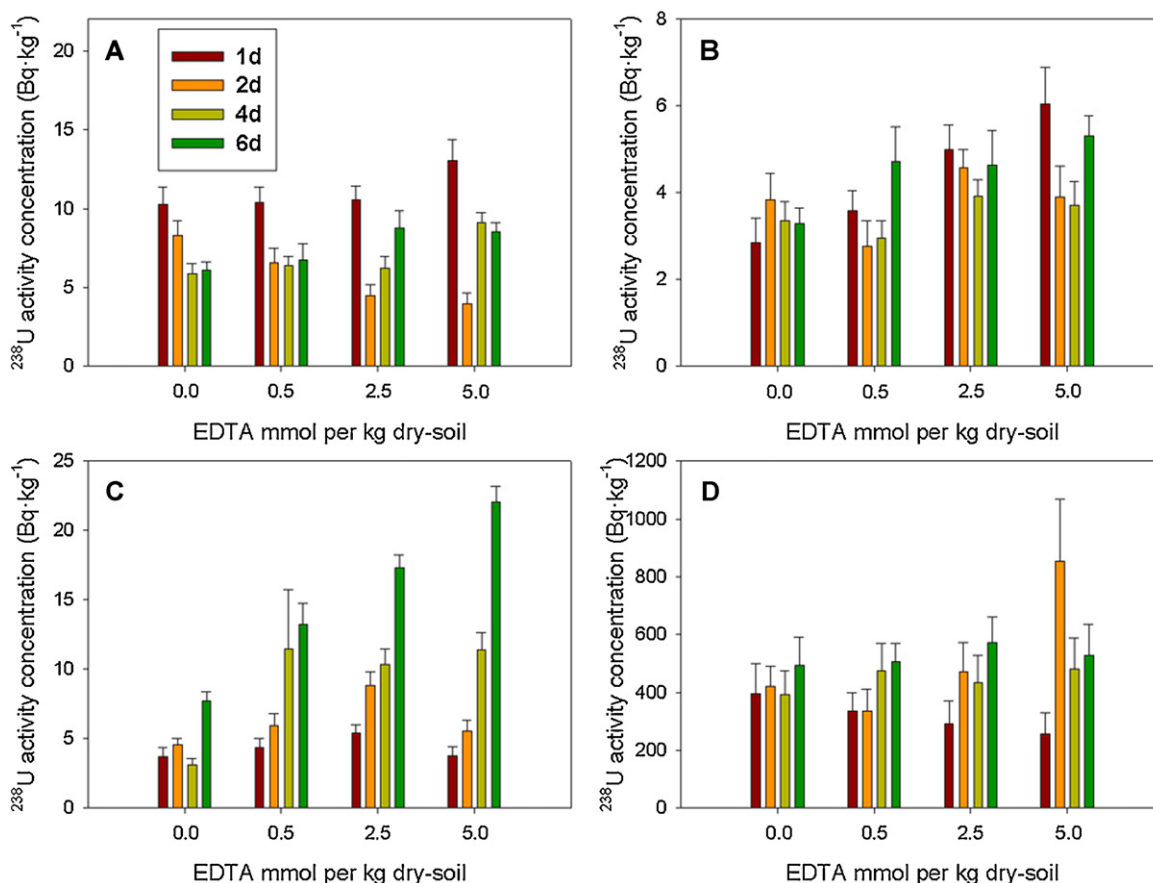


Fig. 5. Variation of the activity concentration of ^{238}U leached with different concentrations of EDTA, for four test times and four pH ranges (as in Fig. 3). The error bars correspond to measurement uncertainties.

3.2.3. EDTA amendment

Fig. 5 shows the results of uranium concentrations of the leachates with the EDTA amendment for the different test times and the pH ranges. As can be seen, the addition of EDTA did not significantly enhance the uranium solubilization, and it is again clear that the most important factor in this solubilization was the pH.

As was noted in Section 3.2.1 (treatment without chelating agents), the greatest uranium solubilization occurs in the alkaline pH range (D) and the uranium extraction efficiency generally increased with longer times. This behaviour was similar with the addition of EDTA.

For the experiments of pH series C, the addition of EDTA improved the uranium solubilization, with clear increases with test time and EDTA concentration, so that the best results corresponded to 5 mmol of EDTA after six days. Nonetheless, this best value was still below 1% of bulk uranium concentration in the soil (3385 Bq kg^{-1}).

The results were even poorer for the experiments of pH series B, with the solubilization of the uranium being very similar to the control.

In the most acidic pH range tested (pH series A), the behaviour with the addition of EDTA was similar to the control. Only the addition of 5 mmol increased the solubilization with respect to the control, but again after the first day some of the previously solubilized uranium was again fixed in the soil.

Although EDTA has proved effective with other metals [44], the present results show that it is unsuitable for uranium solubilization. Similar findings have been reported by other workers. Huang et al. [6] describe unsatisfactory results with the addition of 5 mmol. The explanation may be the unselective nature of EDTA [45], with competition from other cations, such as Fe, Al, Ca or Mg, or high

clay content preventing uranium entering solution [34]. In particular, the efficacy of EDTA is reduced in Ca-rich soils [46], and in the present experiments CaCl_2 was in all cases added to the soil during the incubation period.

The presence of chelating agents enhances the desorption of organic material from the soil matrix as the pH is increased [38,39]. Indeed, in the present experiments, series B, and even more so series C, showed increased extraction of uranium compared to the controls with increasing chelator concentration, and also for the higher pH's.

3.2.4. EDDS amendment

Fig. 6 shows the results for the uranium activity concentrations in solution with the EDDS amendment. Again, the pH determined the uranium solubilization. For each range of pH, the addition of EDDS enhanced the solubilization more effectively than was the case with EDTA amendment, but considerably less than with the addition of citrate.

With no amendment (control), the greatest uranium solubilization occurred at alkaline pH (pH series D). In this series, the addition of EDDS only slightly enhanced the solubilization. It is interesting to note that in this pH series there was a similar irregular pattern of temporal behaviour for all four EDDS concentrations. They all showed a reduction on the second day of treatment, and reached the highest value on the third day. In the other three pH series (A, B, and C), the addition of EDDS significantly enhanced the uranium solubilization with respect to the control, but there was also a rapid reduction with time corresponding to uranium re-absorption, so that the best results in these series corresponded to the early days of treatment.

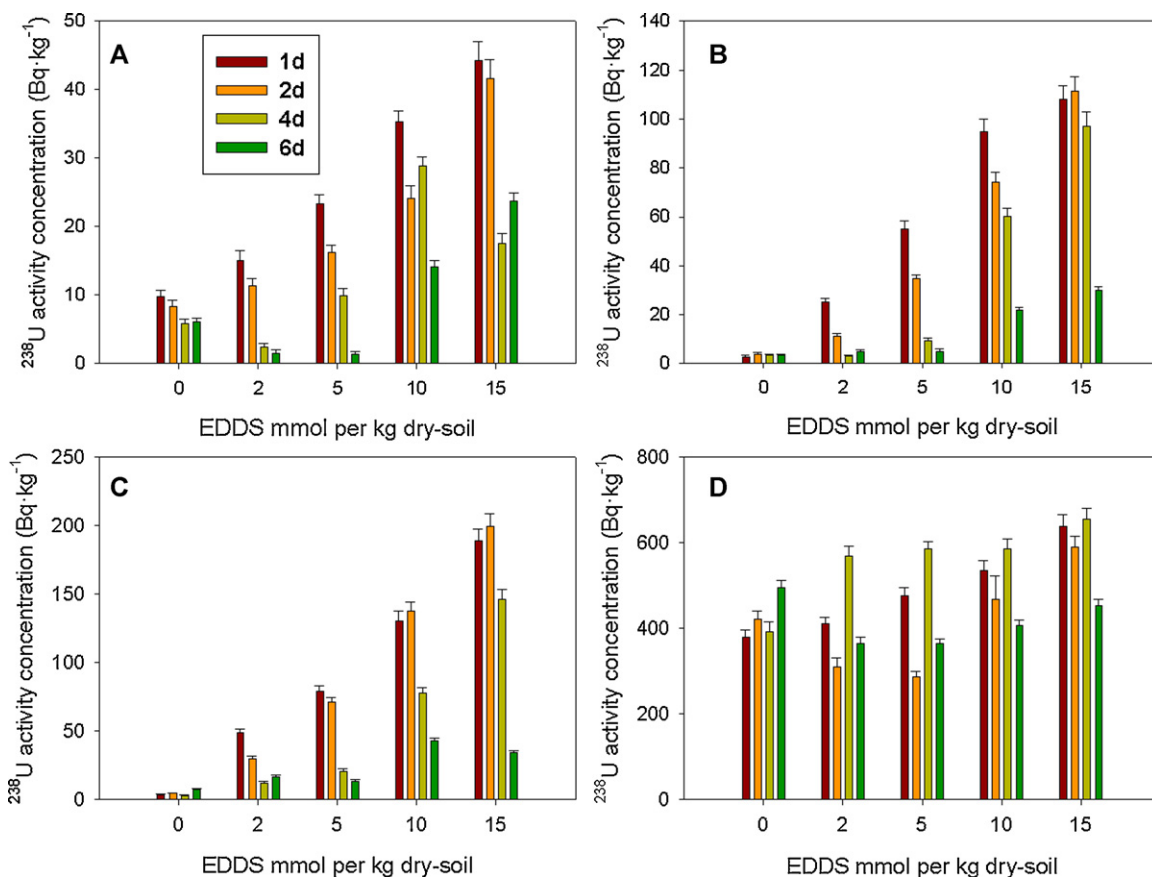


Fig. 6. Variation of the activity concentration of ^{238}U leached with different concentrations of EDDS, for four test times and four pH ranges (as in Fig. 3). The error bars correspond to measurement uncertainties.

The greatest improvement with respect to the control trials was observed in the pH series C (pH: 6.0–6.5) for the greatest EDDS concentration tested (15 mmol) and on the second day of treatment. The solubilization in this case reached 5.9% of bulk uranium concentration in the soil (3385 Bq kg^{-1}).

Compared to EDTA, EDDS was more effective at a less alkaline pH. According to the thermodynamic dissociation constants for the polyprotic ligands EDDS ($\text{pK}_1 = 2.4$, $\text{pK}_2 = 3.9$, $\text{pK}_3 = 6.8$, and $\text{pK}_4 = 9.8$) and EDTA ($\text{pK}_1 = 2.1$, $\text{pK}_2 = 3.0$, $\text{pK}_3 = 6.4$, and $\text{pK}_4 = 10.4$), the reactivity of EDDS is somewhat shifted towards acidity. This was reflected in the pH series B and C in which the EDDS amendment markedly enhanced the uranium solubilization. A further contribution to this effect probably also came from the greater initial concentrations of EDDS than of EDTA.

As was the case with EDTA, the addition of EDDS should enhance the desorption of organic matter in the soil as the pH changes to less acidic conditions [39]. The effects of the presence of EDDS on the uranium extraction were only clearly observed in the series B and C. As was the case with EDTA, the effective reactivity to form complexes with uranium is conditioned by competition with other soil metals [33,39]. A slight increase was observed on the fourth day, followed by a decrease on the sixth day which is likely attributable to the degradation of the ligand. In this series, there were decreases on the second day for initial concentrations of 2 and 5 mmol of EDDS. Such re-adsorption of free and complexed EDDS, and renewed solubilization, have been described by other authors [37,39].

The degradation of EDDS (7–32 days including a lag phase [37]) can explain the systematic reduction of uranium in solution observed with the passage of time. Moreover, the rapid fall in pH at

the end of the test period (Fig. 2c) could contribute to the decrease of uranium in solution by its re-adsorption onto the soil.

4. Conclusions

The most efficient chelating agent to solubilize uranium from a granitic soil was found to be citrate. It was more effective for all four pH ranges tested, and comparatively for all concentrations. This versatility allows the concentration of this agent to be suited to the requirements of different plants and different protocols [33]. In addition, its rapid degradation contributes to the environmental friendliness of its use as an amendment, since its application enhances uranium mobility for a relatively few hours.

Amendment of this granitic soil with EDTA was unsuccessful at solubilizing uranium under any of the conditions tested.

In addition to its degradability, and within its specific levels of phytotolerance, EDDS was found to be somewhat more effective than EDTA at extracting uranium, especially in the pH range tested of slight acidity, coincident with the natural pH of the soil being tested.

Acknowledgments

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